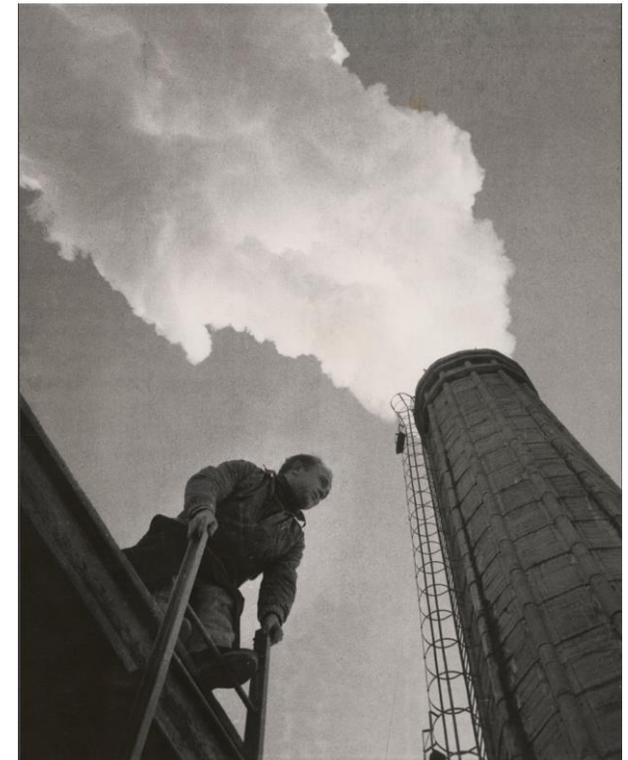
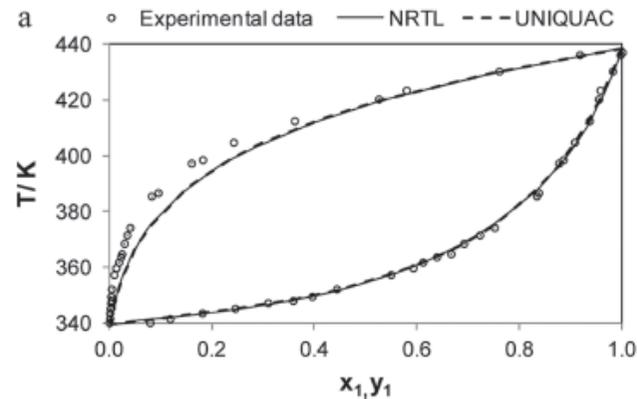
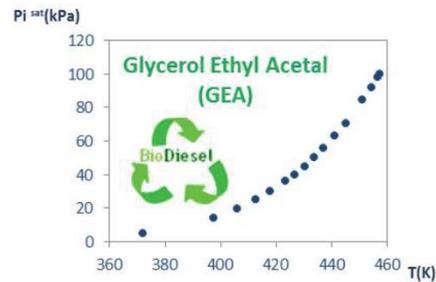


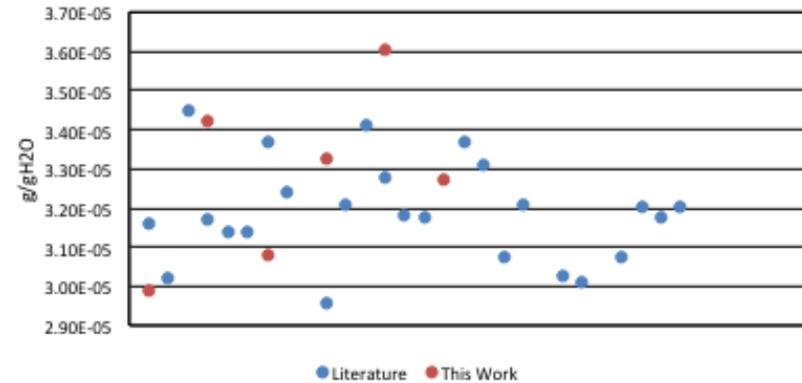
# CONSISTENCY TESTS FOR PHASE EQUILIBRIA AND PROCESS DESIGN



## 1. Motivation

## 2. VLE Tests

- Herington
- Van Ness
- Point
- Infinite Dilution
- Global Analysis



## 3. LLE Methods

- Binary Systems
- Hand and Othmer-Tobias

## 4. SLE Tests

- Eutectic Systems
- Statistical Analysis

## 5. Conclusions



## 1. Data for process and product design:

- Compilation
- Evaluation
- Selection
- Model development

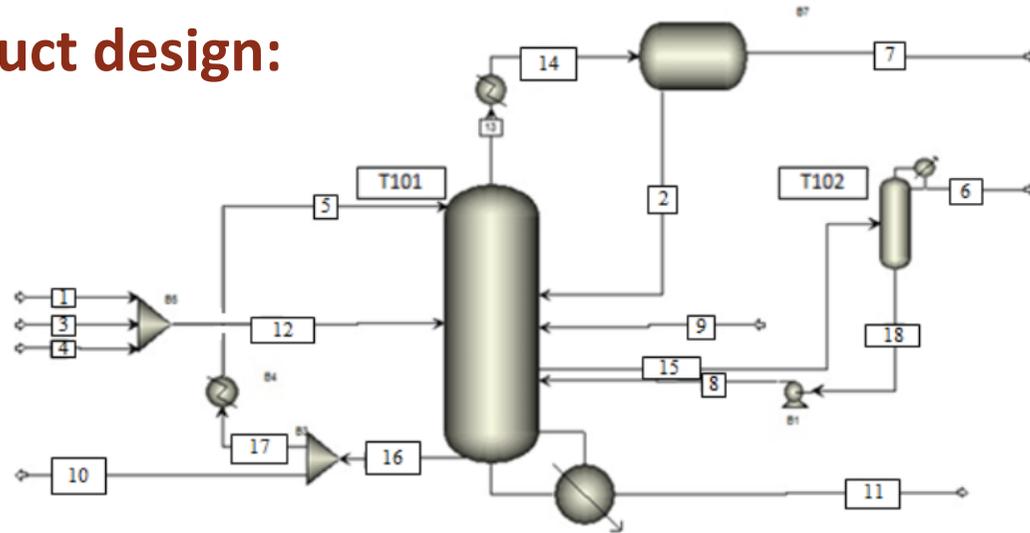


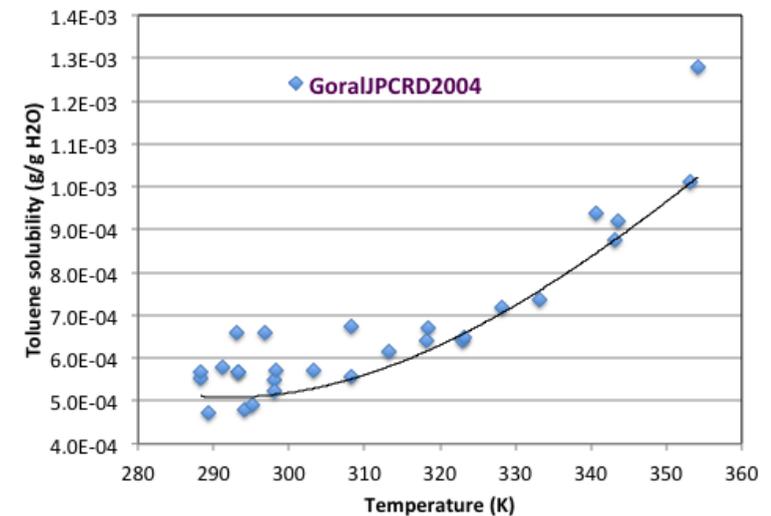
Figure 1. Acrylonitrile recovery system (adapted from an existing unit)

## 2. Quality assessment:

- Experimental planning
- Publication

### Databases

- <http://ddbonline.ddbst.com>
- <http://i-systems.dechema.de/detherm>
- <http://ilthermo.boulder.nist.gov>
- <http://www.aiche.org/dippr>
- <http://dippr.byu.edu/student.asp>
- <http://trc.nist.gov/termolit>



Reis et al. Sep. Sci. Technol. (2016)

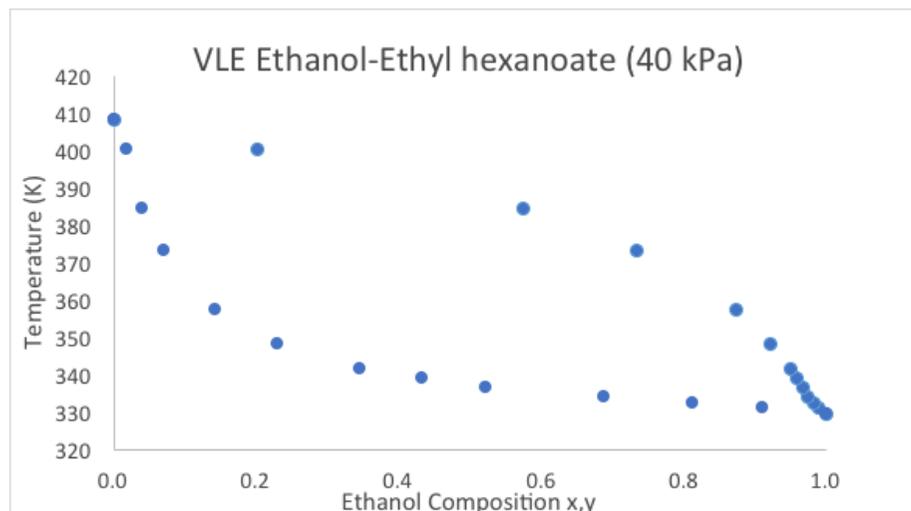
Góral et al. J. Phys. Chem. Ref. Data, 33, 1159-1188 (2004)

- Besides to uncertainties on variables such as pressure, temperature and composition, two more restrictions must be considered:

**Gibbs-Duhem equation**

**Consistency with pure component vapor pressures**

- Many tests have been proposed, but none accepted consensually
- Methodology here selected proposed at NIST (Kang et al., 2010, 2014)



Kang et al. J. Chem. Eng. Data, 55, 3631-3640 (2010)  
Kang et al. J. Chem. Eng. Data, 59, 2283-2293 (2014)

☞ To apply the consistency tests some conditions must be satisfied:

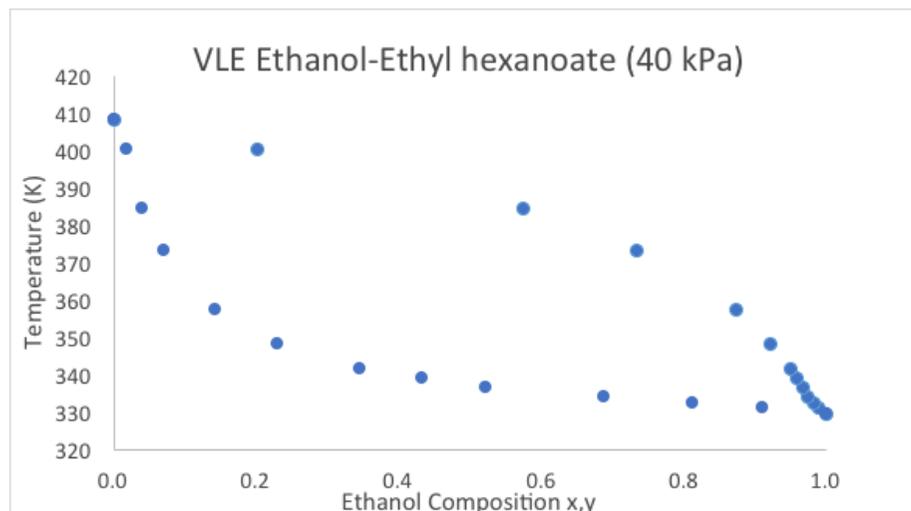
Pure component data is known (vapor pressure, critical data and virial coefficients)

Experimental VLE data is subcritical

The number of experimental data points (excluding pure component data) is at least 5

The studied composition range in mole fraction is higher than 0.5

The largest gap in the liquid mole fraction composition is over than 0.8



From the Gibbs-Duhem equation, at constant pressure or temperature:

$$A^* = \int_0^1 \ln \frac{g_1}{g_2} dx_1 + \int_0^1 e dx_1$$

Where,

$$e = \left( \frac{V^E}{RT} \right) \left( \frac{\partial p}{\partial x_1} \right)_T \quad \text{Constant } T \qquad e = - \left( \frac{H^E}{RT^2} \right) \left( \frac{\partial T}{\partial x_1} \right)_p \quad \text{Constant } p$$

For isothermal VLE data,  $\varepsilon$  can be neglected, but for isobaric data the excess enthalpy dependency with temperature and composition must be known

These difficulties led to use some empirical parameters:

$$D = 100 \left| \frac{A - B}{A + B} \right| \qquad J = 150 \left| \frac{DT_{\max}}{T_{\min}} \right|$$

Being  $A$  the area above the zero line on the plot of  $\ln(\gamma_1/\gamma_2)$  against  $x_1$ , and  $B$  the area below

For the integration of experimental data a polynomial equation of  $d$  order ( $2 < d < 6$ ) is selected based on the correlation coefficient of the fit:

$$y = \sum_{i=1}^{d+1} a_i x_1^{i-1}$$

The quality factor of the Herington test ( $F_{test1}$ ) is obtained by:

$$F_{test1} = 0.25 \frac{5}{D}, \quad 5 \leq D \leq 50 \quad \text{Constant } T$$

$$F_{test1} = 0.25 \frac{10}{|D - J|}, \quad 10 \leq |D - J| \leq 100 \quad \text{Constant } p$$

## Examples:

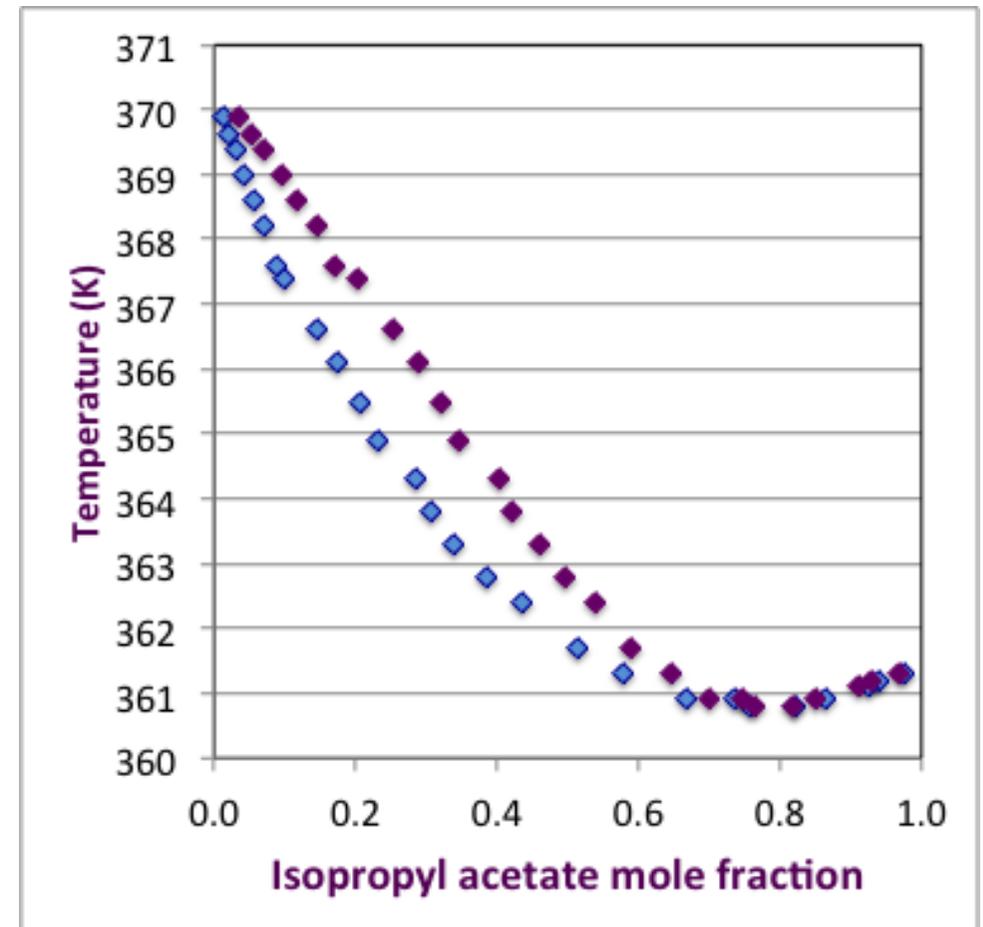
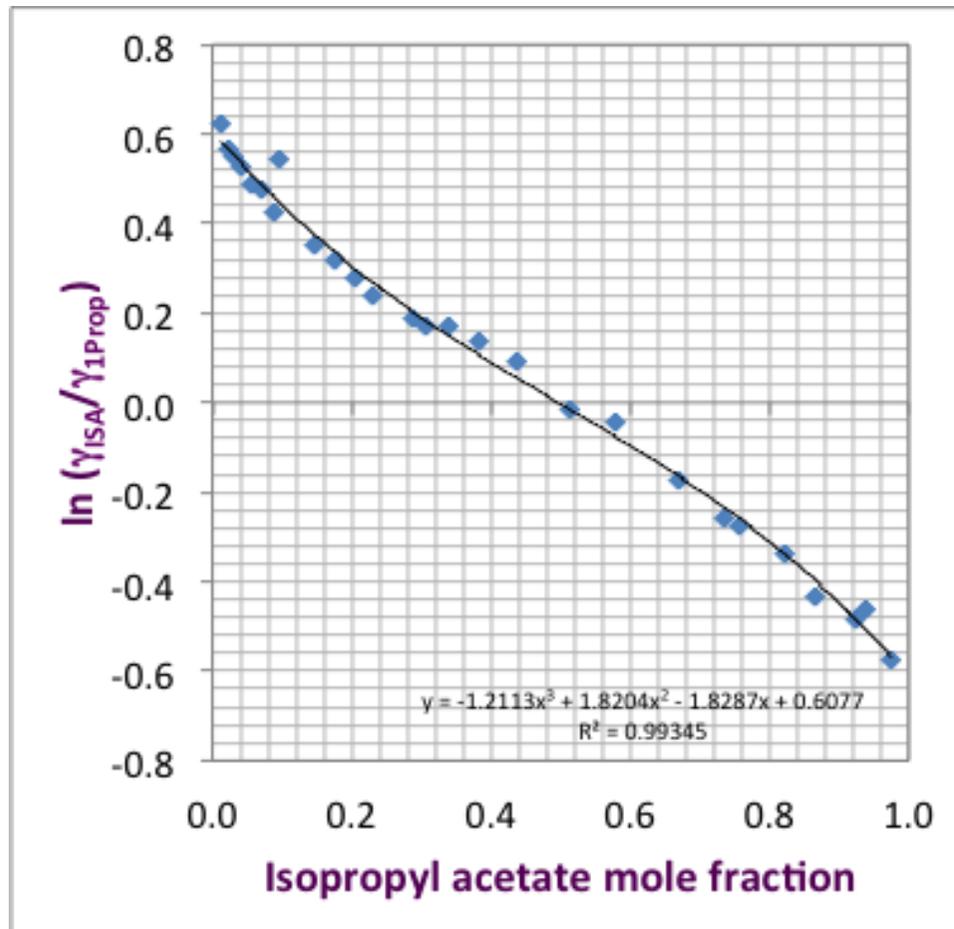
Isopropyl acetate + 1-Propanol at 101.33 kPa (ISA-1Pro)

Ethyl hexanoate + Ethanol at 40 kPa (EH-Eth)

Ethyl octanoate + 1-Pentanol at 15 kPa (EO-1Pen)

## Isopropyl Acetate + 1-Propanol

101.33 kPa

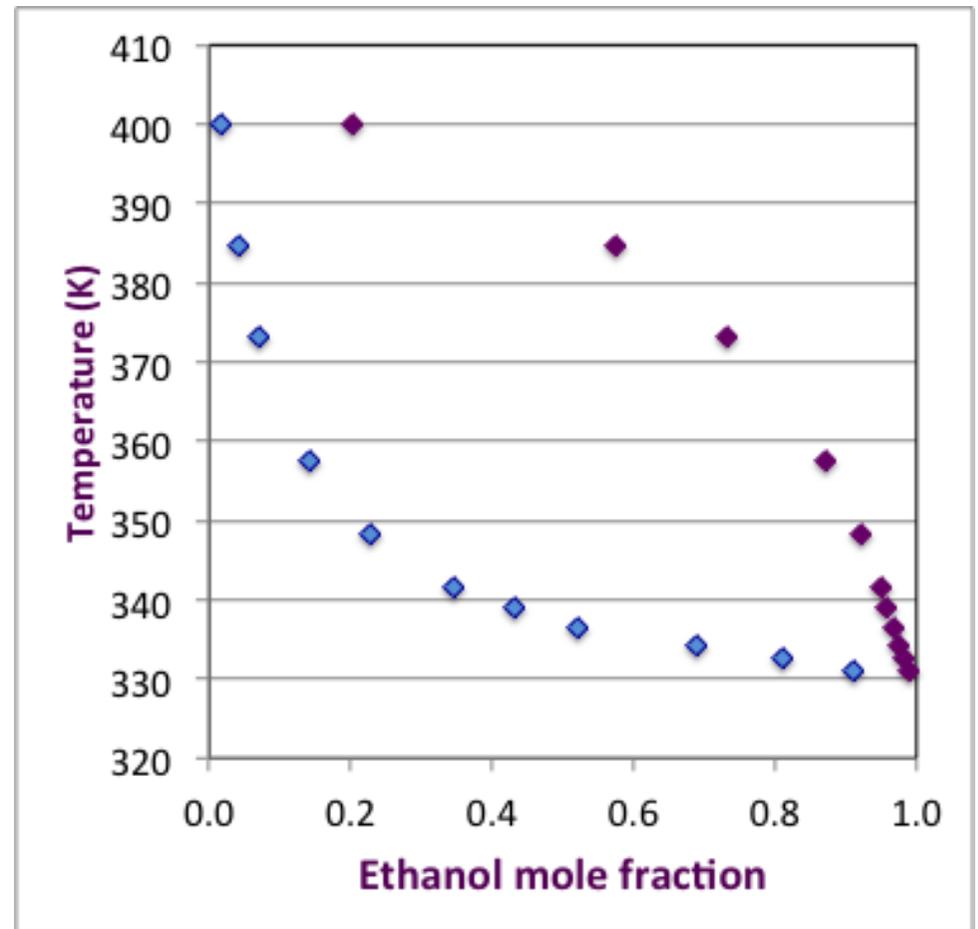
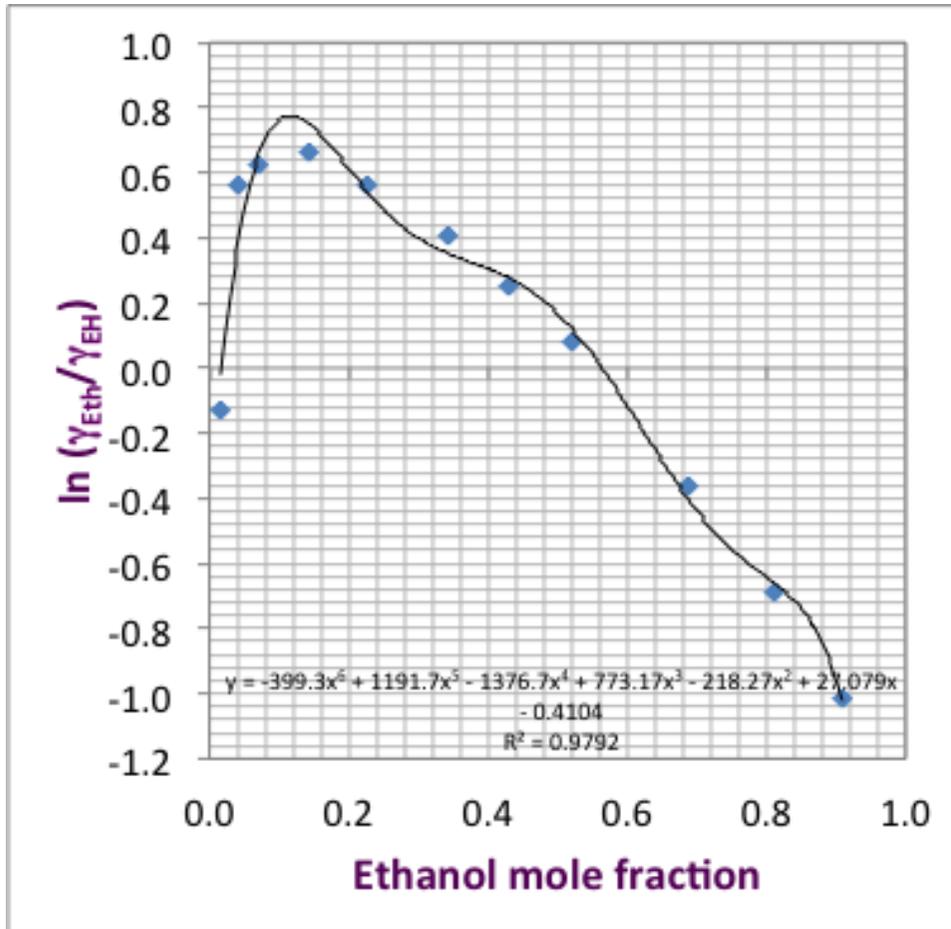


$$|D - J| = 2.90 \quad F_{test1} = 0.25 \frac{10}{|D - J|} = 0.25, \quad 10 \notin |D - J| \notin 100$$

Casimiro et al. J. Chem. Eng. Data, 60, 3181-3186 (2015)

## Ethyl Hexanoate + Ethanol

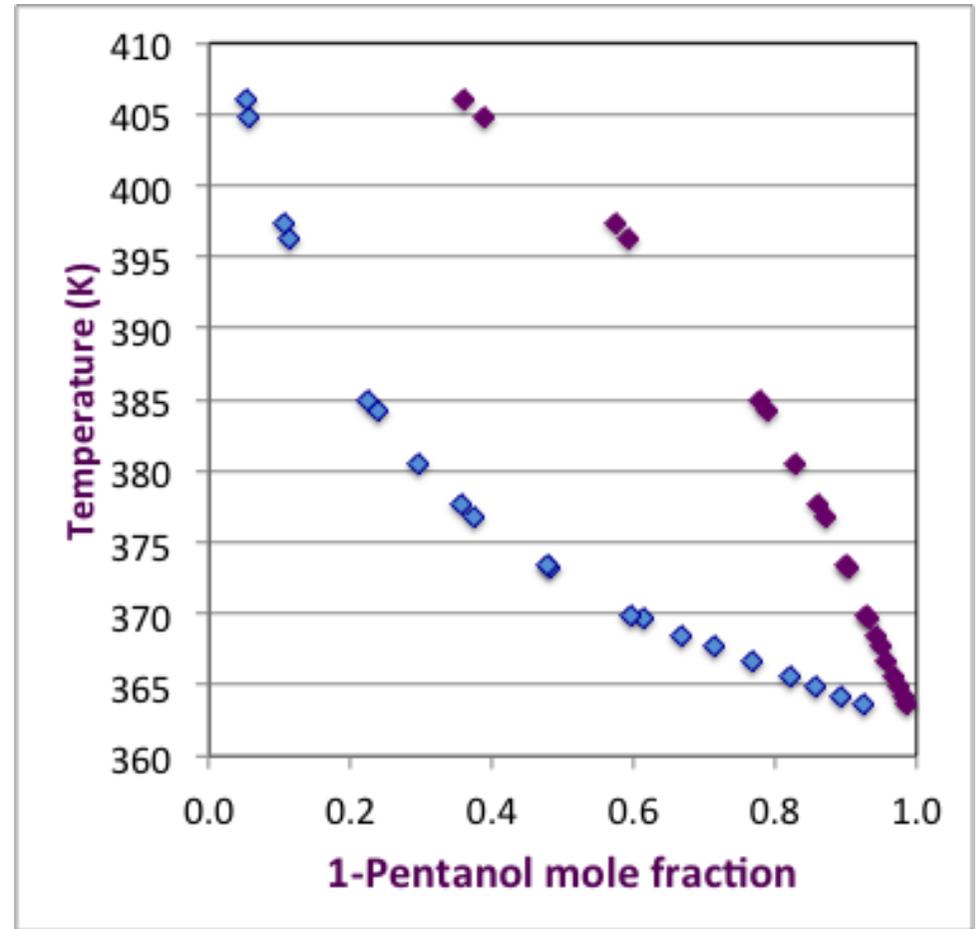
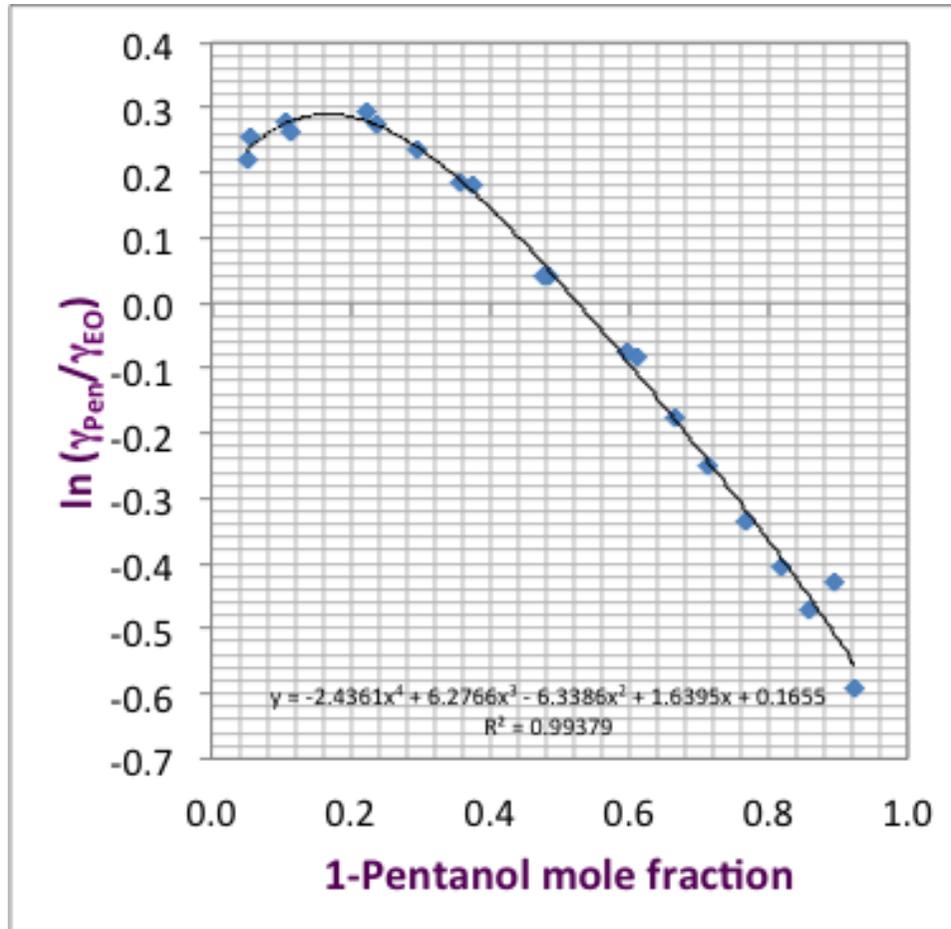
40.00 kPa



$$|D - J| = 8.62 \quad F_{\text{test}1} = 0.25 \frac{10}{|D - J|} = 0.25, \quad 10 \notin |D - J| \notin 100$$

## Ethyl Octanoate + 1-Pentanol

15.00 kPa



$$|D - J| = 16.24 \quad F_{test1} = 0.25 \frac{10}{|D - J|} = 0.15, \quad 10 \notin |D - J| \notin 100$$

Is regarded as a modeling capability test. Using NRTL with:

$$A_{ji} = A_{ji}^A + A_{ji}^B (x_i - x_j) \quad \text{Constant } T$$

$$A_{ji} = A_{ji}^A + A_{ji}^B / T \quad \text{Constant } p$$

After the fitting process the deviations are calculated :  $Dp = \frac{100}{N} \sum_{i=1}^N \left| \frac{p_i^{\text{exp}} - p_i^{\text{calc}}}{p_i^{\text{exp}}} \right|$

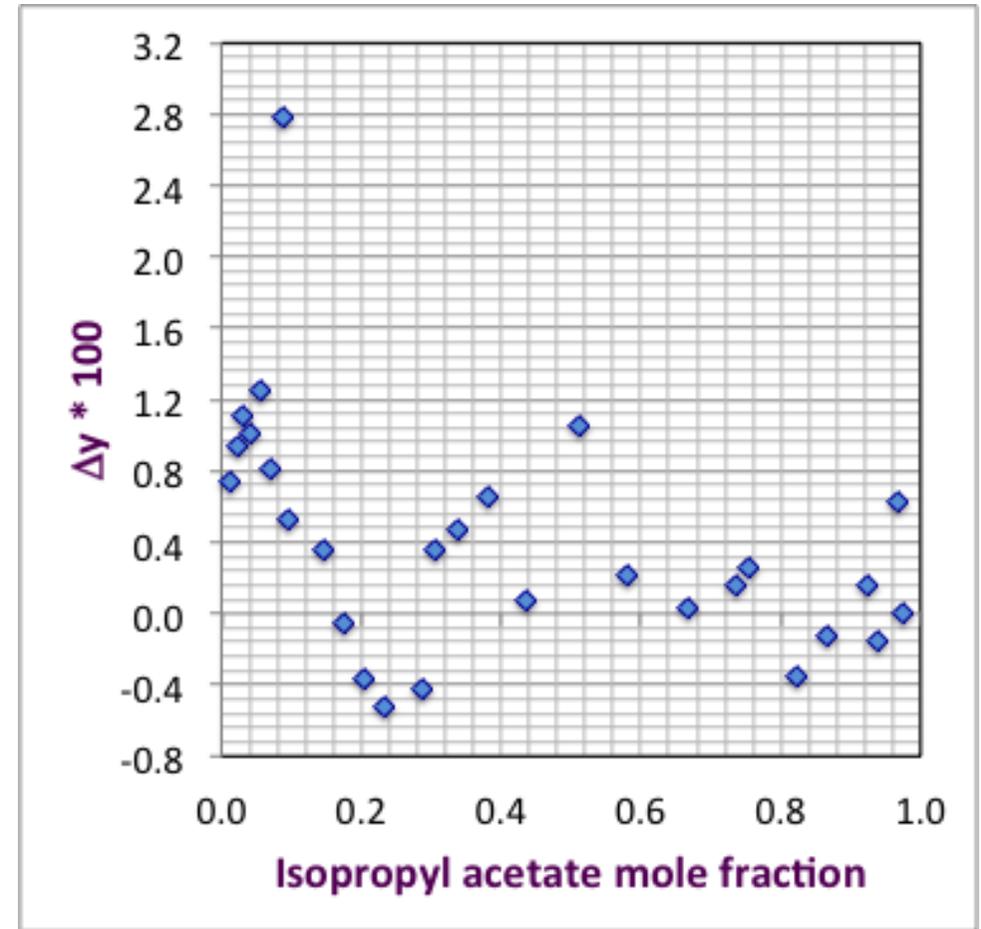
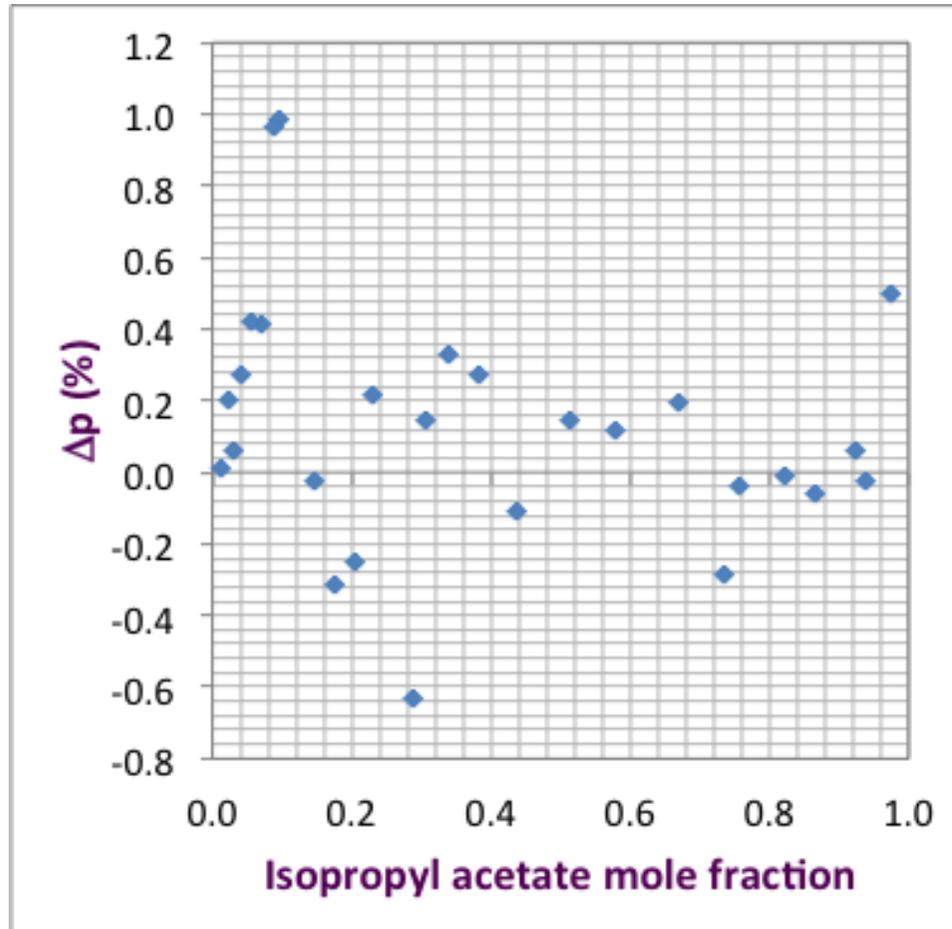
$$Dy = \frac{100}{N} \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{calc}}|$$

The quality factor of the Van Ness test ( $F_{\text{test}2}$ ) is obtained by:

$$F_{\text{test}2} = 0.25 \frac{2}{Dp + Dy}, \quad 1 \leq Dp \leq 10 \quad 1 \leq Dy \leq 10$$

## Isopropyl Acetate + 1-Propanol

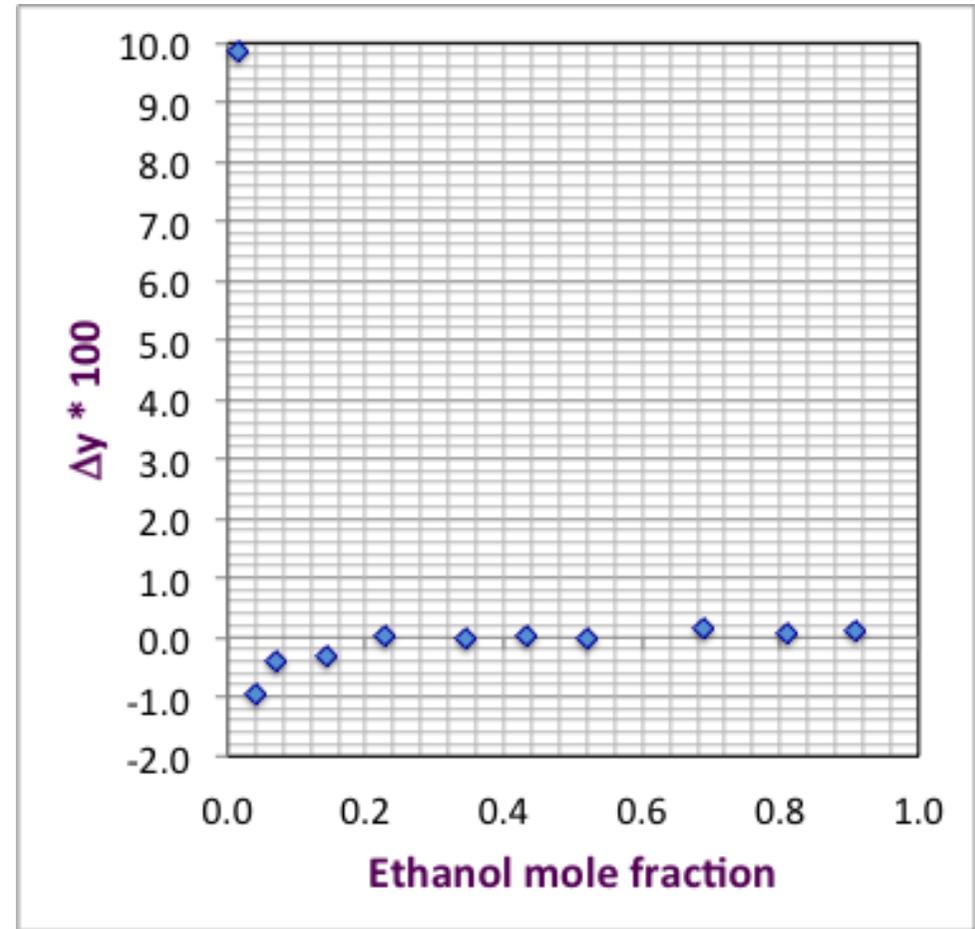
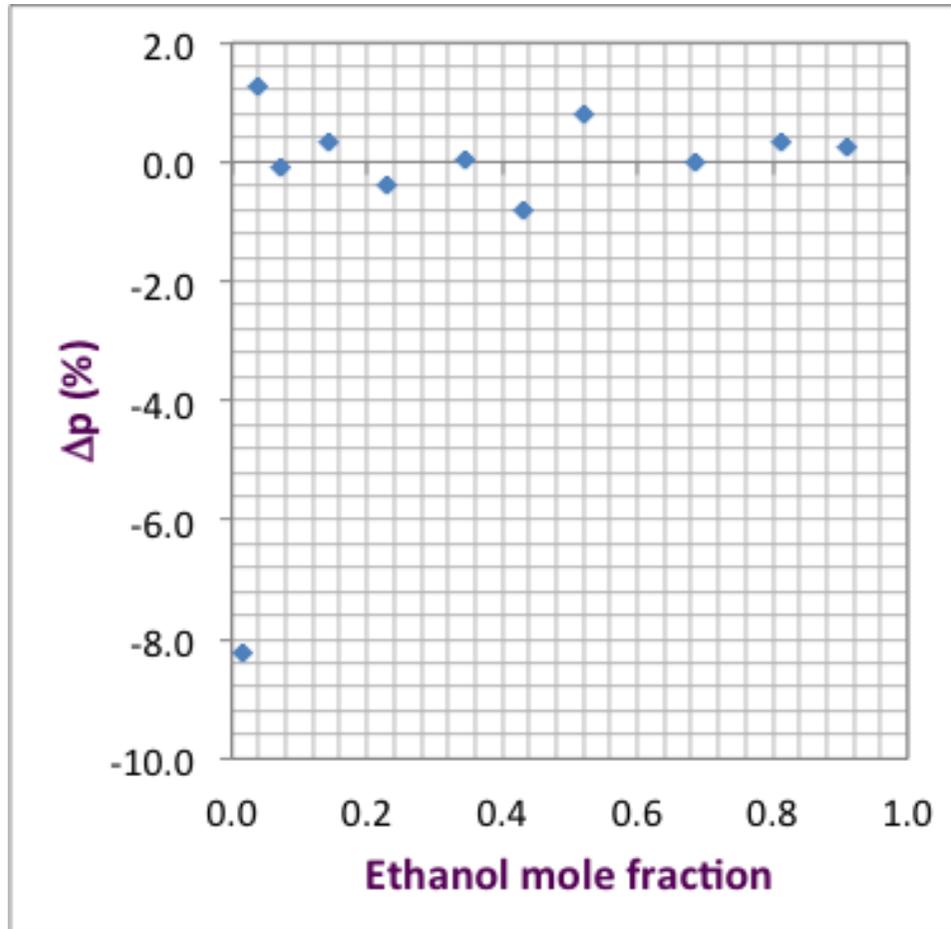
101.33 kPa



$$Dp = 0.12 \quad Dy = 0.41 \quad F_{test2} = 0.25 \frac{2}{Dp + Dy} = 0.25, \quad 1 \leq Dp \leq 10 \quad 1 \leq Dy \leq 10$$

## Ethyl Hexanoate + Ethanol

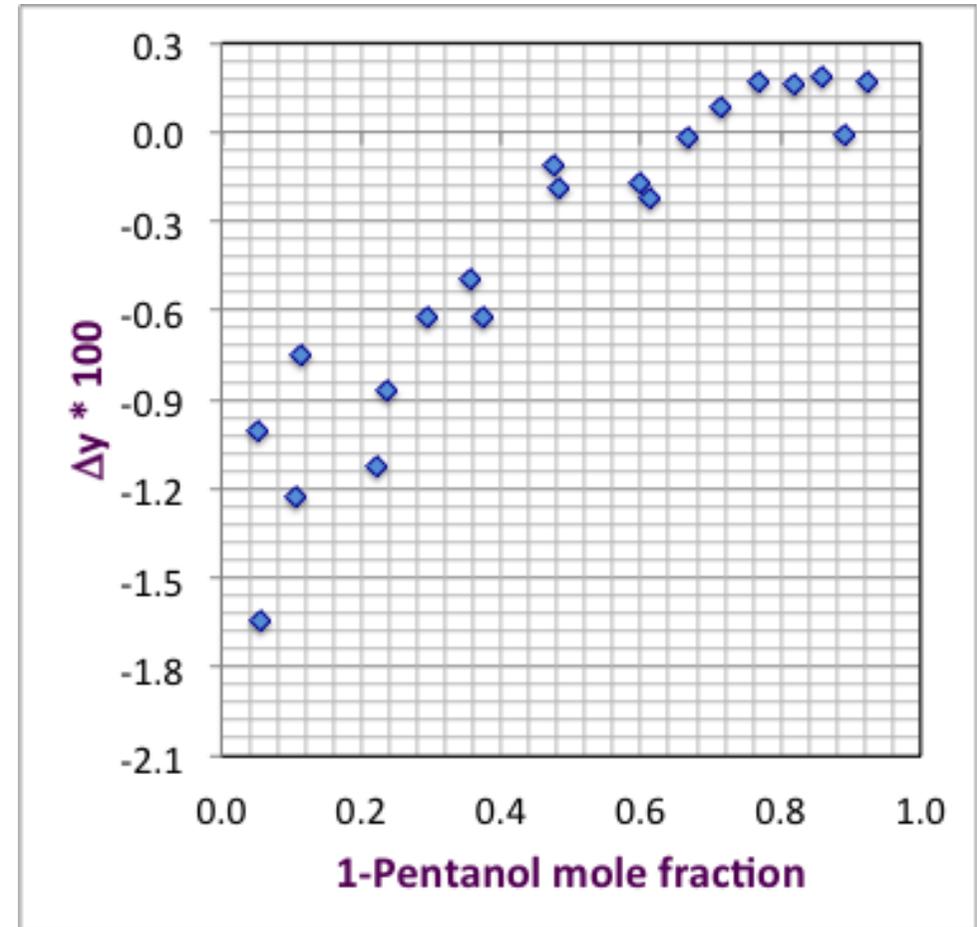
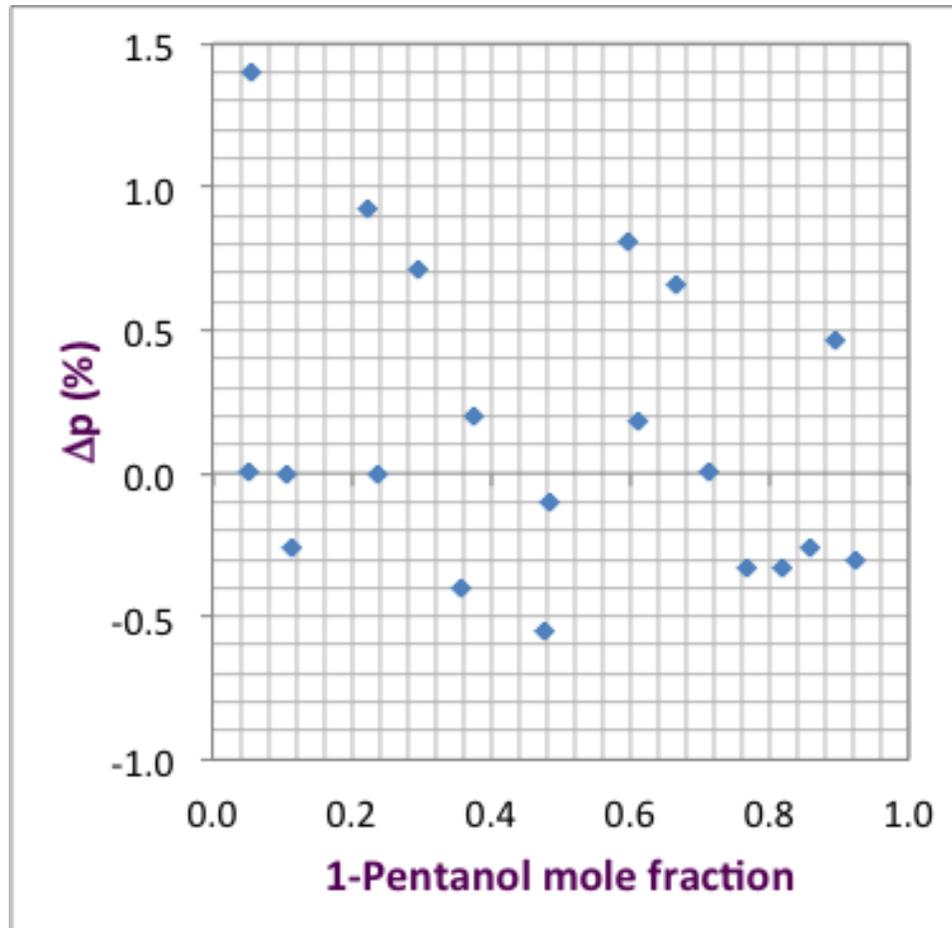
40.00 kPa



$$Dp = 1.14 \quad Dy = 1.08 \quad F_{test2} = 0.25 \frac{2}{Dp + Dy} = 0.23, \quad 1 \leq Dp \leq 10 \quad 1 \leq Dy \leq 10$$

## Ethyl Octanoate + 1-Pentanol

15.00 kPa



$$Dp = 0.39 \quad Dy = 0.49 \quad F_{test2} = 0.25 \frac{2}{Dp + Dy} = 0.25, \quad 1 \leq Dp \leq 10 \quad 1 \leq Dy \leq 10$$

From experimental  $p$ - $T$ - $x$ - $y$  data the calculated activity coefficients are used to obtain the  $G^E/RT$ , which is fitted to a Padé approximation ( $M = 1$  and  $N = 3$ )

$$\frac{G^E}{RT} = x_1 x_2 \frac{a_0 + \sum_{n=1}^N a_n (x_1 - x_2)^n}{1 + \sum_{m=1}^M b_m (x_1 - x_2)^m}$$

For each experimental data point:  $d_k^* = \left[ \frac{d(G^E/RT)}{dx_1} - \ln\left(\frac{g_1}{g_2}\right) \right]_k$

And,

$$d = \frac{100}{N} \sum_{k=1}^N d_k^*$$

The quality factor of the point test ( $F_{test3}$ ) is obtained by:

$$F_{test3} = 0.25 \frac{5}{d}, \quad 5 \leq d \leq 50$$

Is a test for the limiting behavior of excess Gibbs energy and the activity coefficients. The following parameters are calculated:

$$I_1 = 100 \left| \frac{G^E / (RTx_1x_2) - \ln(g_1/g_2)}{\ln(g_1/g_2)} \right|_{x_1=0}$$
$$I_2 = 100 \left| \frac{G^E / (RTx_1x_2) + \ln(g_1/g_2)}{\ln(g_1/g_2)} \right|_{x_2=0}$$

The quality factor of the point test ( $F_{\text{test 4}}$ ) is given by:

$$F_{\text{test 4}} = 0.25 \frac{60}{I_1 + I_2}, \quad 30 \leq I_1, I_2 \leq 300$$

Kojima et al. Fluid Phase Equilib., 56, 269-284 (1990)

Kurihara et al. Fluid Phase Equilib., 219, 75-85(2004)

## Infinite dilution activity coefficients

Compounds	$G^E/RTx_1x_2$	$\ln(\gamma_1/\gamma_2)$	$I_j$	$F_{test4}$
Isopropyl Acetate	1.64	1.74	11.2	
1-Propanol	1.82	1.71	11.3	0.25
Ethyl Hexanoate	3.92	3.73	3.8	
Ethanol	1.11	1.38	67.4	0.15
Ethyl Octanoate	1.85	2.04	11.3	
1-Pentanol	0.81	1.17	243.2	0.05

$$F_{test4} = 0.25 \frac{60}{I_1 + I_2}, \quad 30 \leq I_1, I_2 \leq 300$$

In the case that pure compound vapor pressures are not measured, they can be estimated from  $p$ - $T$ - $x$ - $y$  data:

$$p_{bubble}(x_1 \rightarrow 1) = P_1^{sat} \quad e \quad p_{bubble}(x_1 \rightarrow 0) = P_2^{sat}$$
$$p_{dew}(y_1 \rightarrow 1) = P_1^{sat} \quad e \quad p_{dew}(y_1 \rightarrow 0) = P_2^{sat}$$

Defining:

$$Dp_j^{sat} = \left| \frac{p_{bubble}(x_j \rightarrow 1) - P_j^{sat}}{P_j^{sat}} \right| \quad or \quad Dp_j^{sat} = \left| \frac{p_{dew}(x_j \rightarrow 1) - P_j^{sat}}{P_j^{sat}} \right|$$

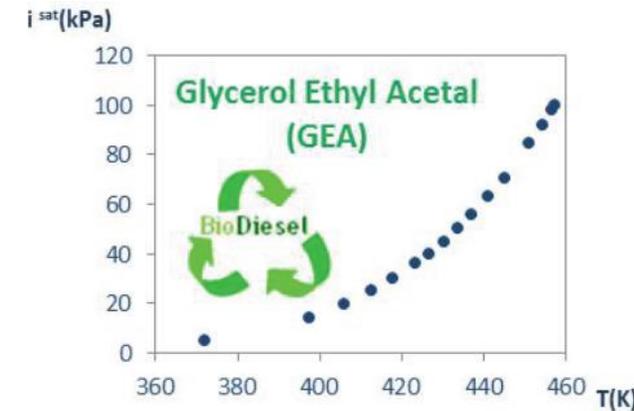
The quality factor of the point test ( $F_{puro}$ ) is given by:

$$F_{puro} = \frac{2}{100(Dp_1^{sat} + Dp_2^{sat})}, \quad 1 \leq Dp_1^{sat}, Dp_2^{sat}$$

The global quality factor of the VLE dataset ( $Q_{VLE}$ ) is given by:

$$Q_{VLE} = F_{puro} (F_{test1} + F_{test2} + F_{test3} + F_{test4}), \quad Q_{VLE} \leq 1$$

Systems	$F_{test1}$	$F_{test2}$	$F_{test4}$	$F_{pure}$	Overall	NIST
Isopropyl Acetate						
1-Propanol	0.25	0.25	0.25	1.00	1.00	0.88
Ethyl Hexanoate						
Ethanol	0.25	0.23	0.15	1.00	0.84	0.76
Ethyl Octanoate						
1-Pentanol	0.15	0.25	0.05	1.00	0.58	0.58



Wisniak (1994) proposed: 
$$J = 150 \left| \frac{H_{average}^E}{G_{max}^E} \right| \left| \frac{DT_{max}}{T_{min}} \right|$$

Van Ness, penalize experimental data when the model is not able of fitting them. NRTL model is accurate but is not of “reference quality”

Wisniak, *J. Ind. Eng. Chem. Res.*, **33**, 177-180 (1994)  
 Constantino et al. *J. Chem. Eng. Data*, **58**, 1717-1723(2013)  
 Marcilla et al. *Ind. Eng. Chem. Res.*, **52**, 13198-13208 (2013)  
 Mathias, P. M. *Ind. Eng. Chem. Res.*, **55** 1076-1087 (2016)

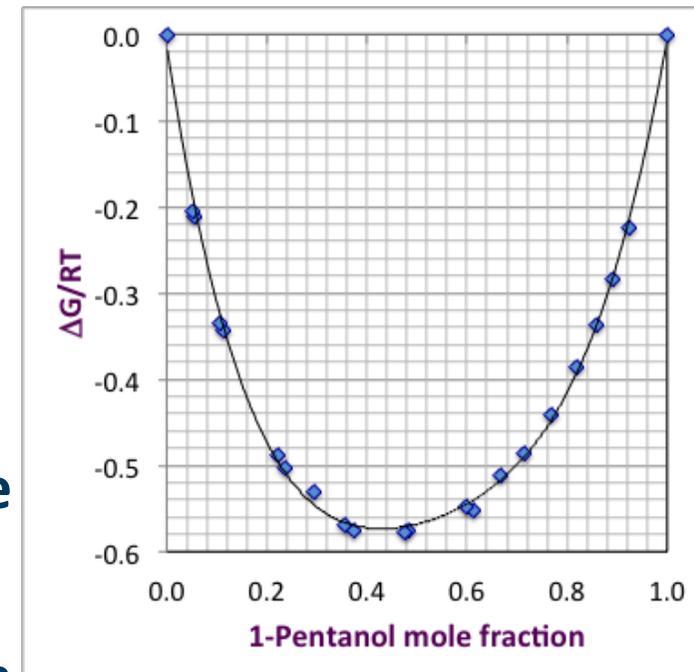
## 1. Some other strategies:

- 📄 Cross-check between infinite dilution activity coefficients and VLE
- 📄 Cross-check between excess enthalpy and VLE
- 📄 Prediction with UNIFAC
- 📄 Represent the Gibbs energy of mixing
- 📄 Random distribution on errors

Compounds	$G^E/RTx_1x_2$	$\ln(\gamma_1/\gamma_2)$	UNIFAC-Do
Ethyl Hexanoate	3.92	3.73	4.20
Ethanol	1.11	1.38	1.53
Ethyl Octanoate	1.85	2.04	1.86
1-Pentanol	0.81	1.17	1.15

## 2. Anomalies:

- 📄 Overall VLE factor less than 0.05
- 📄 Average absolute deviation in temperature greater than 10 K
- 📄 Average absolute deviation in composition greater than 0.05



At a constant pressure, the Gibbs-Duhem equation for each phase (I or II) for a binary liquid-liquid phase-equilibrium is:

$$x_1' d \ln g_1' + x_2' d \ln g_2' + \frac{H^{E,I}}{RT^2} dT = 0$$

$$x_1'' d \ln g_1'' + x_2'' d \ln g_2'' + \frac{H^{E,II}}{RT^2} dT = 0$$

Again, it is not possible to apply due to enormous lack of excess enthalpy data in both liquid phases. Additionally, compositions of both liquid phases are not bind by those equations.

However, the dependence of liquid phase compositions on temperature, at constant pressure, should be continuous over both liquid phases, what can be used for quality assessment.

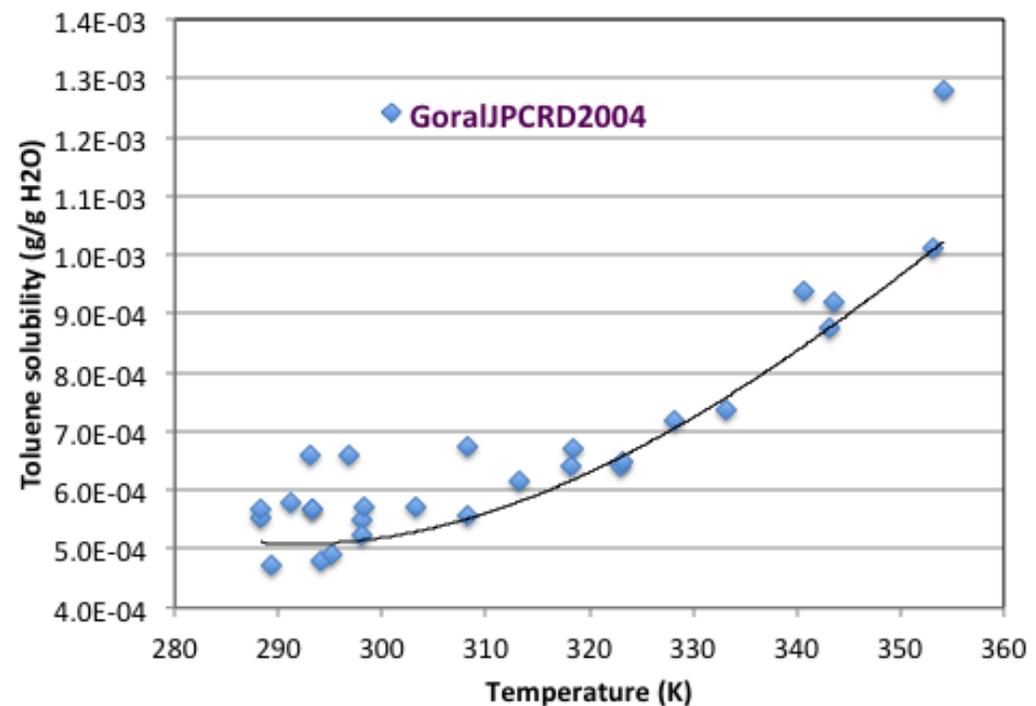
The extent of experimental data and system type defines the analytical representation of LLE.

A few examples:

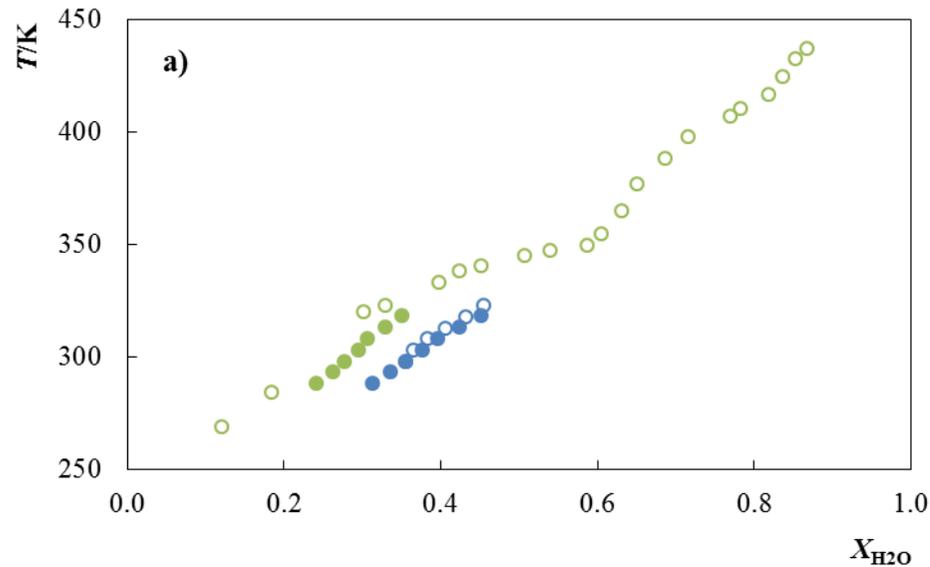
$$T / K = A_0 + A_1/x_1 + A_2/x_2 + \sum_{i=3}^8 A_i (x_1 - x_2)^i$$

$$\ln x_1 = (c_1 + c_2 b) + (c_3 + c_4 b) \left[ \left( T_{\min} / T \right) \ln \left( T_{\min} / T \right) + 1 - T_{\min} / T \right]$$

- Equation is selected based on the quality of the fit
- Statistical analysis of random (not systematic) errors
- Experimental data is rejected based on a conventional 3-sigma rejection considering the local data quality expected for each value
- Rejection of data can go up to 30%



Góral et al. *J. Phys. Chem. Ref. Data*, 33, 1159-1188 (2004)  
Chirico et al. *Pure and Appl. Chem.*, 81, 791-828 (2009)



## (a) Ionic liquid rich phase

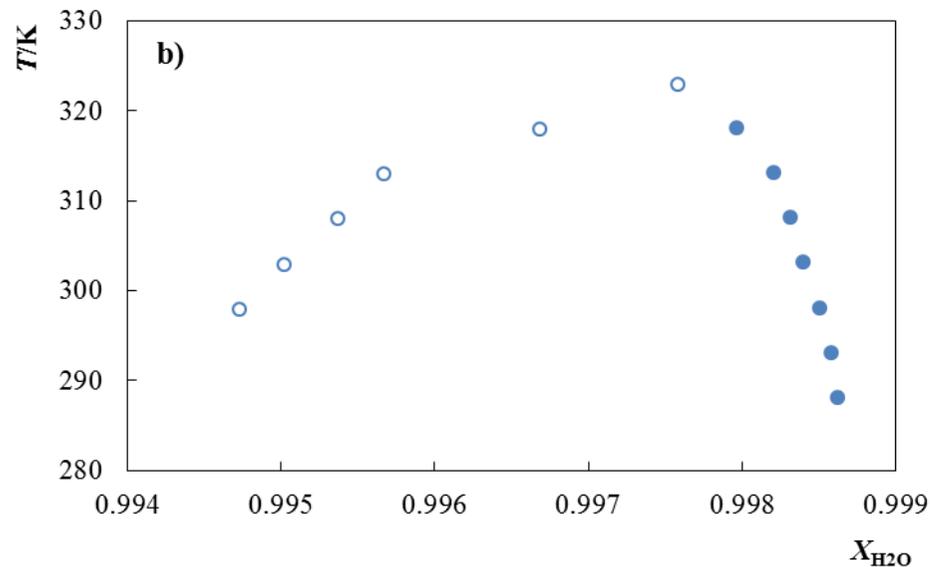
Symbols:

(●), [C<sub>1</sub>C<sub>1</sub>im][NTf<sub>2</sub>] this work

(○), [C<sub>1</sub>C<sub>1</sub>im][NTf<sub>2</sub>] Gardas et al. (2010)

(●), [C<sub>2</sub>C<sub>2</sub>im][NTf<sub>2</sub>] this work

(○), [C<sub>2</sub>C<sub>2</sub>im][NTf<sub>2</sub>] Domańska et al. (2008)



## (b) Water rich phase

Symbols:

(●), [C<sub>1</sub>C<sub>1</sub>im][NTf<sub>2</sub>] this work

(○), [C<sub>1</sub>C<sub>1</sub>im][NTf<sub>2</sub>] Gardas et al. (2010)

Domańska et al. *J. Chem. Eng. Data*, **53**, 1126-1132 (2008)

Gardas et al. *Fluid Phase Equilib.*, **294**, 139-147 (2010)

Martins et al. *Fluid Phase Equilib.*, **375**, 161-167 (2014)

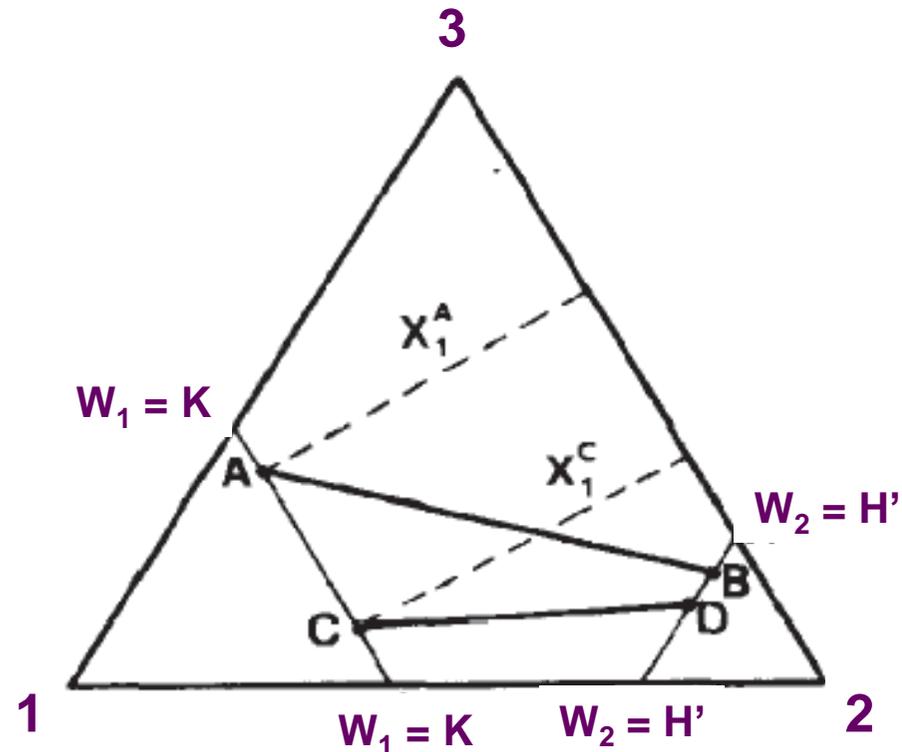
Consistency of tie-line data in ternary systems can be checked by the Hand and Othmer-Tobias empirical equations:

$$\ln\left(\frac{w_{32}}{w_{22}}\right) = k_H \ln\left(\frac{w_{31}}{w_{11}}\right) + c_H$$

$$\ln\left(\frac{1 - w_{22}}{w_{22}}\right) = k_{OT} \ln\left(\frac{1 - w_{11}}{w_{11}}\right) + c_{OT}$$

Hand equation is derived assuming 1 and 2 are almost immiscible, while component 3 is at low concentration in both phases.

Geometrically Othmer-Tobias correlation can be presented as:



Carniti et al. *Fluid Phase Equilib.*, 2, 39-47 (1978)

- It was also numerically shown these equations are insensitive to additive, multiplicative or random errors
- Are too insensitive to be used for consistency tests
- Are useful to check whether experimental data have a regular trend
- Othmer-Tobias** correlation is better to identify high random errors
- Hand** correlation is useful for estimating the location of the plait point

Ideas recently developed for SLE consistency checks under attention

A methodology similar to the established for VLE has been proposed for SLE

**Both component activities can not be obtained simultaneously**

**Pure component melting point are less well-known**

**Typical models not as reliable as for VLE**

The large majority of binary systems composed of organic compounds form eutectics, and not solid solutions

The solubility of a solid in a liquid can be calculated by:

$$\ln(g_j x_j) = -\frac{DH_{m,j}}{RT_{m,j}} \left( \frac{T_{m,j}}{T} - 1 \right) + \frac{DC_P}{R} \left( \frac{T_{m,j}}{T} - 1 + \ln \frac{T}{T_{m,j}} \right)$$

So, the following criteria should be met: *If  $x_j \rightarrow 0$  then  $T \rightarrow T_{m,j}$*

$$\lim_{x_j \rightarrow 0} \left( \frac{dx_j}{dT} \right)_{eq\ ES} = \lim_{x_j \rightarrow 0} \left( \frac{dx_j}{dT} \right)_{exp}$$

The limiting slope is estimated with SLE data for mole fraction ranging from 0 to 0.2 and 0.8 to 1. The following equation is suggested:

$$\ln x_j = A + BT + C \ln T$$

For the melting temperature the quality factor is:

$$DT_{m,j} = |T_{m,\text{exp}} - T_{m,\text{corr}}|$$

$$F_{j,T_m} = \frac{0.5}{DT_{m,j}} \quad \text{if} \quad DT_{m,j} > 0.5$$

For the slope:

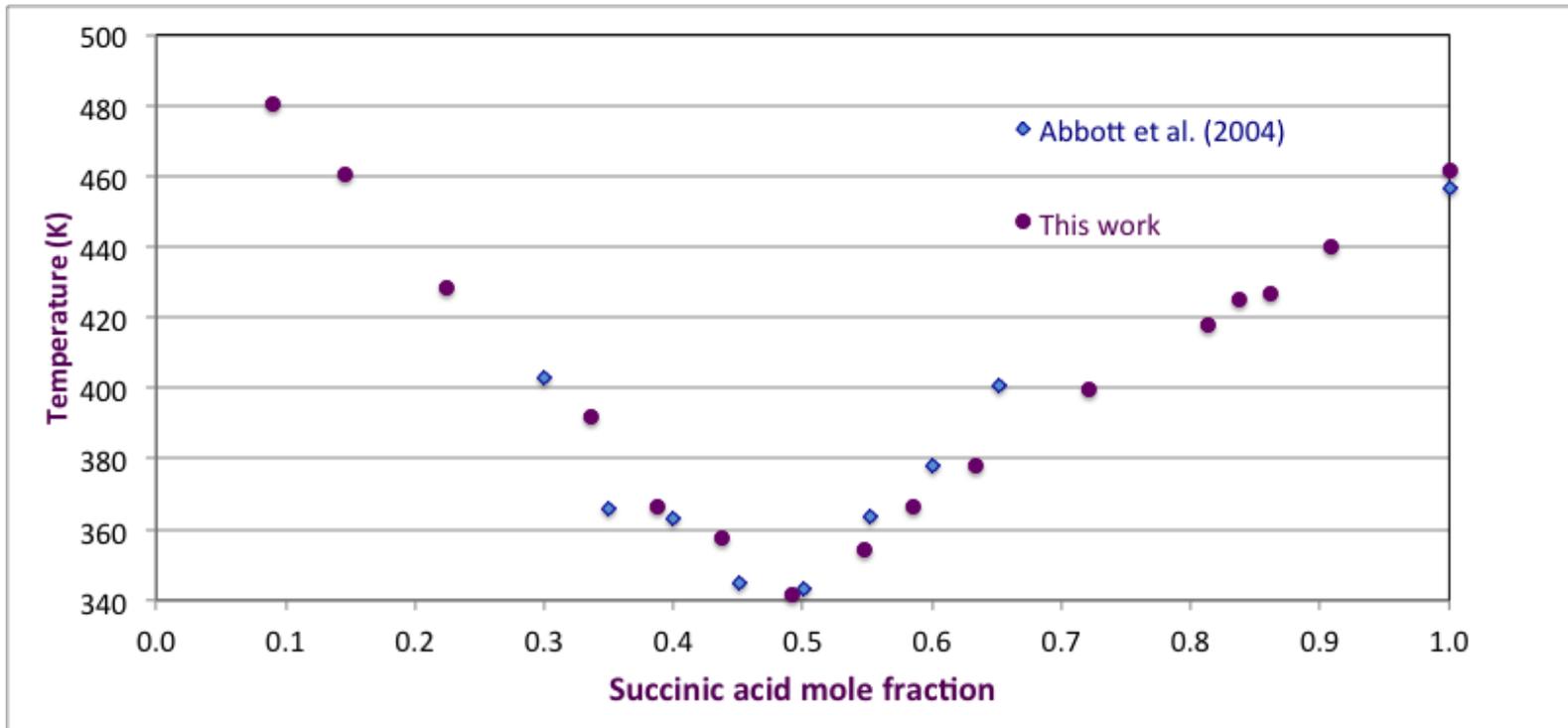
$$Dslope_j = \left| \lim_{x_i \rightarrow 0} \left( \frac{dx_j}{dT} \right)_{\text{eq ESL}} - \lim_{x_i \rightarrow 0} \left( \frac{dx_j}{dT} \right)_{\text{exp}} \right|$$

$$F_{j,\text{slope}} = 1 \quad \text{if} \quad Dslope_j \leq 0.02$$

$$F_{j,\text{slope}} = \frac{0.02}{Dslope_j} \quad \text{if} \quad Dslope_j > 0.02$$

The global SLE quality factor is:

$$Q_{SLE} = 0.25F_{1,T_m} + 0.25F_{2,T_m} + 0.25F_{1,\text{slope}} + 0.25F_{2,\text{slope}}$$



$$F_{SA, T_m} = 1.0$$

$$F_{SA, slope} = 1.0$$

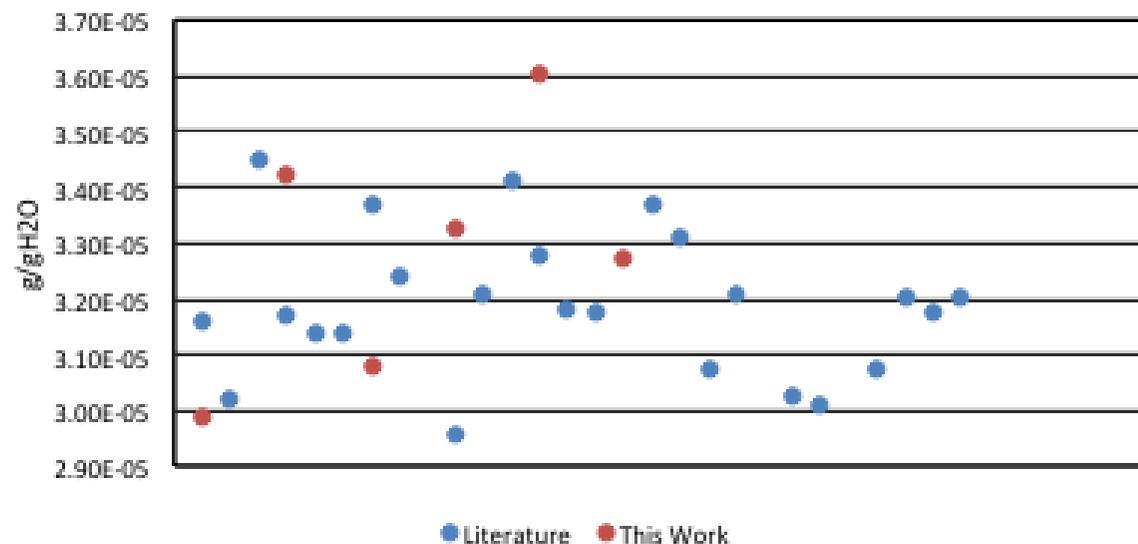
Pure compound melting temperatures

Fluctuation solution theory for assess model fitting capabilities

Abbott et al. J. Am. Chem. Soc., 126, 9142-9147 (2004)

Cunico et al. Fluid Phase Equilib., 362, 318-327 (2014)

## Naphthalene



### (a) This work

Average:  $3.22E-05 \text{ g/g}_{H_2O}$

Standard deviation/average: 6.8%

Extended uncertainty:  $2.73E-06 \text{ g/g}_{H_2O}$

### (b) Literature

Average:  $3.19E-05 \text{ g/g}_{H_2O}$

Lower limit:  $2.96E-05 \text{ g/g}_{H_2O}$

Upper limit:  $3.45E-05 \text{ g/g}_{H_2O}$

Martins et al., Submitted to Chemosphere, 2016

Yalkowsky et al., 2010, Handbook of Aqueous Solubility Data, 2nd edition, CRC Press

- ❑ Several methods were presented and applied to assess VLE data. Different methods give quite different results, but their combination can give important information about data quality.
- ❑ The importance of combine VLE data with other experimental and predicted information was shown.
- ❑ Experimental LLE data for binary systems was analyzed based on empirical correlations showing the difficulties associated to those methods.
- ❑ Hand and Othmer-Tobias equations were shown to be insensitive to several type of errors, and their general use to test ternary LLE data was put into question.
- ❑ The tests for SLE consistency data analysis are under development, but seem to be very promising.
- ❑ Validation of experimental methodologies can be performed also by some statistics.
- ❑ Generally a lot of work is still needed, in particular for LLE consistency studies.

# Acknowledgments

IFP Seminar April 2016



*“Les beautés qu’on découvre plus tôt son aussi celles dont on se fatigue le plus vite.”*

Marcel Proust



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